

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

⦿ BLACK BORDERS

- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-290616

(43)Date of publication of application : 05.11.1993

(51)Int. CI.

H01B 1/06

H01M 6/18

(21)Application number : 04-115337

(71)Applicant : MITSUBISHI CABLE IND LTD

(22)Date of filing : 07.04.1992

(72)Inventor : KUBOTA SHUJI

(54) SOLID ELECTROLYTE

(57)Abstract:

PURPOSE: To provide a solid electrolyte made of a polysiloxane group film having excellent ionic conductivity and stable quality.

CONSTITUTION: A solid electrolyte comprises an alkaline metallic salt-containing hydrophilic ether group oligomer contained in the micro-domain of a film made of polysiloxane having a hydrophobic radical and a hydrophilic radical. The polysiloxane film of micro-phase separation structure can consequently be formed, and consequently the alkaline metallic salt-containing ether group oligomer can be retained in the hydrophilic phase of the polysiloxane film, so that ions may be efficiently transported by the active segmenting movement of polysiloxane, the promotion of ion transport via the hydrophilic radical, and the ethereal group oligomer retained in the micro-domain of the film.

LEGAL STATUS

[Date of request for examination] 30.03.1999

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3335665

[Date of registration] 02.08.2002

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998, 2003 Japan Patent Office

(19)日本国特許庁(JP)

(12) 公開特許公報(A)

(11)特許出願公開番号

特開平5-290616

(43)公開日 平成5年(1993)11月5日

(51)Int.Cl. ⁵	発明記号	庁内整理番号	FI	技術表示箇所
H01B 1/06		A 7244-5G		
H01M 6/18		E		

審査請求 未請求 請求項の数1(全3頁)

(21)出願番号 特願平4-115337

(22)出願日 平成4年(1992)4月7日

(71)出願人 000003263

三菱電線工業株式会社

兵庫県尼崎市東向島西之町8番地

(72)発明者 久保田 修司

兵庫県尼崎市東向島西之町8番地 三菱電
線工業株式会社内

(74)代理人 弁理士 藤本 勉

(54)【発明の名称】 固体電解質

(57)【要約】

【目的】 イオン伝導度に優れて品質の安定したポリシロキサン系の膜からなる固体電解質を得ること。

【構成】 疎水基と親水基を有するポリシロキサンからなる膜中にアルカリ金属塩含有の親水性エーテル系オリゴマーを含有することを特徴とする固体電解質。

【効果】 ミクロ相分離構造のポリシロキサン膜を形成できてその親水相にアルカリ金属塩含有のエーテル系オリゴマーを保有させることができ、ポリシロキサンの活発なセグメント運動と、その親水基によるイオン輸送の助長と、ミクロドメインに保有されたエーテル系オリゴマーが効率よくイオン輸送する。

(2)

特開平5-290616

1

【特許請求の範囲】

【請求項1】 疎水基と親水基を有するポリシロキサンからなる膜中に、アルカリ金属塩含有の親水性エーテル系オリゴマーを含有することを特徴とする固体電解質。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、イオン伝導性に優れて薄型電池等の形成に好適な固体電解質に関する。

【0002】

【従来の技術】従来、側鎖にエチレンオキシドのオリゴマーを導入したポリメチルシロキサンからなる膜中にアルカリ金属塩を含有させてなる固体電解質が知られていた。しかしながら、イオン伝導性に劣る問題点があった。

【0003】

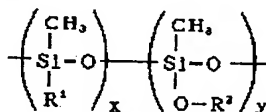
【発明が解決しようとする課題】本発明は、イオン伝導性に優れて品質の安定したポリシロキサン系の膜からなる固体電解質の開発を課題とする。

【0004】

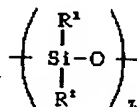
【課題を解決するための手段】本発明は、疎水基と親水基を有するポリシロキサンからなる膜中に、アルカリ金属塩含有の親水性エーテル系オリゴマーを含有することを特徴とする固体電解質を提供するものである。

【0005】

(I)



(II)



【0008】前記の一般式において、R¹は、炭素数が3個以上のアルキル基やフェニル基などからなる疎水基である。R²は、末端メチル化ポリエチレンオキシド基、末端メチル化ポリプロピレンオキシド基、末端メチル化エチレンオキシド・プロピレンオキシド共重合体基（ランダム共重合体、ブロック共重合体）、水酸基、カルボキシル基、アミノ基、スルホ基などからなる親水基である。

【0009】前記の親水基としては、エーテル系ポリマーの結晶化の抑制によるイオン伝導度の向上などの点より、-X-CH₂や-Y-CH₂（ただしXは(CH₂)_n、H₂O、Yは(CH₂)_nCH(CH₂)O、である。）で表される末端メチル化ポリエチレンオキシド基や末端メチル化ポリプロピレンオキシド基、あるいは末端メチル化エチレンオキシド・プロピレンオキシド共重合体基などが好ましい。なお式中におけるポリエチレンオキシドやポリプロピレンオキシドの重合度m、nは、2~20が一般的であるがこれに限定されない。

【0010】ポリシロキサンからなる膜中に含ませるアルカリ金属塩含有の親水性エーテル系オリゴマーとして

*【作用】疎水基と親水基を有するポリシロキサンを製膜するとその疎水基と親水基が作用してマイクロ相分離構造を有する膜を形成でき、これにアルカリ金属塩含有の親水性エーテル系オリゴマーを含有させると膜中のマイクロ相分離構造における親水相にアルカリ金属塩含有の親水性エーテル系オリゴマーを保有する膜を形成でき、この膜はイオン伝導性に優れた固体電解質を構成する。その優れたイオン伝導性は、マトリクスポリマーとしてのポリシロキサンの活発なセグメント運動と、その親水基によるイオン輸送の助長と、マイクロドメインに保有されたエーテル系オリゴマーがイオン輸送に充分なスペースで連続的に存在するためであると考えられる。

【0006】

【実施例】本発明の固体電解質は、ポリシロキサン系の膜中にアルカリ金属塩含有の親水性エーテル系オリゴマーを有してなる。膜を形成するポリシロキサンとしては、側鎖に疎水基と親水基を有するものが用いられる。

【0007】前記のポリシロキサンの例としては、次の一般式(I)や(II)で表される構造単位を有するものなどがあげられる。かかるポリシロキサンは例えば化学的重合法や電解重合法などにより形成することができ、その平均分子量は2万~800万が一般的であるがこれに限定されない。

は適宜なものを用いることができる。その例としては、エチレンオキシドオリゴマー、プロピレンオキシドオリゴマー、エチレンオキシド・プロピレンオキシド共重合オリゴマーなどがあげられる。用いる親水性エーテル系オリゴマーの平均分子量は100~20000が一般的であるが、これに限定されない。

【0011】アルカリ金属塩の例としては、Liイオン、Naイオン、Kイオン等の陽イオンと、Iイオン、CF₃SO₃イオン、BF₄イオン、ClO₄イオン、AlCl₄イオン、PF₆イオン、AsF₆イオン、SCNイオン等の陰イオンとの組合せからなるものなどがあげられる。

【0012】固体電解質の形成は例えば、ジメチルアセトアミドの如き極性溶媒を用いて疎水基と親水基を有するポリシロキサンと親水性エーテル系オリゴマーとアルカリ金属塩を溶解させ、その溶液を用いてキャストニング方式等の適宜な方式で製膜することにより行うことができる。その場合、アルカリ金属塩は、予め親水性エーテル系オリゴマーに必要に応じて有機溶媒を用いて溶解させ、その溶液をポリシロキサン溶液中に混合して溶解さ

(3)

特開平5-290618

3

せる方式が、アルカリ金属塩を親水性エーテル系オリゴマー中に集約させる点より好ましい。

【0013】親水性エーテル系オリゴマーの使用量は、使用目的等に応じて適宜に決定してよいが一般にはポリシロキサン100重量部あたり10～200重量部、就中20～100重量部とされる。またアルカリ金属塩の使用量も、目的とするイオン伝導度などに応じて適宜に決定でき、一般には親水性エーテル系オリゴマー100重量部あたり、1～50重量部が用いられる。形成する膜厚は任意であり、通例10～500 μ mである。得られた膜は、固体電解質として電池などの種々の製品の形成に用いることができる。

【0014】実施例1

上記した一般式(1)においてR¹がフェニル基で、R¹がポリエチレンオキシド部分の重合度(m)が2、4、6又は8の末端メチル化ポリエチレンオキシド基であり、R¹を有する部分の重合数(x)が3であり、R¹を有する部分の重合数(y)が1である重量平均分子量約200万のポリシロキサンをジメチルアセトアミドに溶解させ、これにポリシロキサン100重量部あたり30重量部、60重量部又は100重量部のエチレンオキシドオリゴマー(重量平均分子量約400)の配合割合となるようLiClO₄含有のエチレンオキシドオリゴマーの粘稠溶液を攪拌混合して均一溶液を調製し、キャスト

ング方式で厚さ50 μ mの膜を形成して固体電解質を得 *

*た。なおLiClO₄は、エチレンオキシドオリゴマー中のO/Liの原子比が10となる量を用いた。

【0015】比較例

上記した一般式(1)においてR¹を有する部分の重合数(x)が0の、従ってR¹を有する部分のみからなり、そのポリエチレンオキシド部分の重合度(m)が2、4、6又は8の末端メチル化ポリエチレンオキシド基である重量平均分子量約200万のポリシロキサンをジメチルアセトアミドに溶解させ、それにポリシロキサンに導入したR¹のポリエチレンオキシド中のO/Liの原子比が10となるようLiClO₄を攪拌混合して均一溶液を調製し、それを用いて実施例1に準じ固体電解質を得た。従ってこのものは、エチレンオキシドオリゴマーを含有しないものである。

【0016】評価試験

実施例1、比較例で得た固体電解質について交流インピーダンスアナライザーによりイオン伝導度を測定した。その結果を表1に示した。なお表中のA/Bは、ポリシロキサン/エチレンオキシドオリゴマーの割合を意味する。また導入ポリエチレンオキシドの重合度は、ポリシロキサンに導入した末端メチル化ポリエチレンオキシド基におけるポリエチレンオキシド部分の重合度を意味する。

【0017】

【表1】

イオン伝導度 (S/cm; 25℃)					
	A/B	導入ポリエチレンオキシドの重合度			
		2	4	6	8
実施例1	10/3	1/10 ⁶	5/10 ⁶	1/10 ⁵	2/10 ⁴
	10/6	8/10 ⁶	1/10 ⁵	1/10 ⁴	1/10 ³
	10/10	1/10 ⁵	4/10 ⁵	6/10 ⁴	7/10 ³
比較例	10/0	2/10 ⁷	6/10 ⁷	3/10 ⁶	2/10 ⁵

【0018】

【発明の効果】本発明によれば、マイクロ相分離構造のポリシロキサン膜を形成できてその親水性にアルカリ金属

塩含有のエーテル系オリゴマーを保有させることができ、イオン伝導度に優れた品質の安定した固体電解質を得ることができる。

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The solid electrolyte characterized by containing the hydrophilic ether system oligomer of alkali-metal salt content in the film which consists of a polysiloxane which has a hydrophobic group and a hydrophilic group.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention is excellent in ionic conductivity, and relates to the suitable solid electrolyte for formation of a thin shape cell etc.

[0002]

[Description of the Prior Art] Conventionally, the solid electrolyte which makes it come to contain an alkali-metal salt in the film which consists of a poly methyl siloxane to which the oligomer of ethylene oxide was introduced into the side chain was known. However, the trouble of being inferior to ionic conductivity is *****.

[0003]

[Problem(s) to be Solved by the Invention] this invention makes a technical problem development of a solid electrolyte which consists of a film of the polysiloxane system by which was excellent in ionic conductivity and quality was stabilized.

[0004]

[Means for Solving the Problem] The solid electrolyte characterized by this invention containing the hydrophilic ether system oligomer of alkali-metal salt content in the film which consists of a polysiloxane which has a hydrophobic group and a hydrophilic group is offered.

[0005]

[Function] If the polysiloxane which has a hydrophobic group and a hydrophilic group is produced, the film which the hydrophobic group and hydrophilic group act and has micro phase separation structure can be formed, if this is made to contain the hydrophilic ether system oligomer of alkali-metal salt content, the film which holds the hydrophilic ether system oligomer of alkali-metal salt content in the hydrophilic phase in the micro phase separation structure in a film can be formed, and this film constitutes the solid electrolyte which is excellent in ionic conductivity. It is thought that the outstanding ionic conductivity is because the active segmental motion of the polysiloxane as matrix polymer, promotion of the ion transport by the hydrophilic group, and the ether system oligomer held by the micro domain exist continuously in sufficient space for an ion transport.

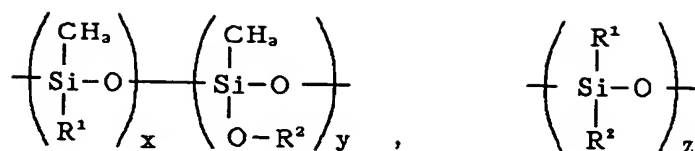
[0006]

[Example] The solid electrolyte of this invention comes to have the hydrophilic ether system oligomer of alkali-metal salt content in the film of a polysiloxane system. As a polysiloxane which forms a film, what has a hydrophobic group and a hydrophilic group is used for a side chain.

[0007] What has the structural unit expressed with the following general formula (I) and (II) as an example of the aforementioned polysiloxane is raised. This polysiloxane can be formed by for example, the chemical polymerization method, the electrolytic polymerization method, etc., and although 20,000-8 million are common as for the average molecular weight, it is not limited to this.

(I)

(I I)



[0008] In the aforementioned general formula, R1 is a hydrophobic group which a carbon number becomes from three or more alkyl groups, phenyl groups, etc. R2 is a hydrophilic group which consists of an end methylation polyethylene-oxide machine, an end methylation polypropylene-oxide machine, an end methylation ethylene oxide propylene-oxide copolymer machine (a random copolymer, block copolymer), a hydroxyl group, a carboxyl group, an amino group, a sulfonic group, etc.

[0009] As the aforementioned hydrophilic group. The end methylation polyethylene-oxide machine expressed with -X-CH3 or -Y-CH3 (however, X is m (CH2CH2O) and Y is n (CH2CH(CH3)O)), an end methylation polypropylene-oxide machine or an end methylation ethylene oxide propylene-oxide copolymer machine, etc. is more desirable than points, such as improvement in the ionic conductivity by suppression of crystallization of ** and ether system polymer. In addition, although 2-20 are common as for the polymerization degree m and n of the polyethylene oxide in a formula, or a polypropylene oxide, it is not limited to this.

[0010] A thing proper as hydrophilic ether system oligomer of the alkali-metal salt content included in the film which consists of a polysiloxane can be used. As the example, ethylene oxide oligomer, propylene-oxide oligomer, ethylene oxide propylene-oxide copolymerization oligomer, etc. are raised. Although 100-2000 are common as for the average molecular weight of the hydrophilic ether system oligomer to be used, it is not limited to this.

[0011] As an example of an alkali-metal salt, what consists of combination with anions, such as cations, such as Li ion, Na ion, and K ion, I ion and CF3SO3 ion, BF4 ion, ClO4 ion, AlCl4 ion, PF6 ion, AsF6 ion, and SCN ion, is raised.

[0012] Formation of a solid electrolyte can dissolve the polysiloxane and the hydrophilic ether system oligomer which have a hydrophobic group and a hydrophilic group using the polar solvent like a dimethylacetamide, and an alkali-metal salt, and can be performed by producing a film by the method with a proper casting method etc. using the solution. In this case, an alkali-metal salt has the method more desirable than the point of making an alkali-metal salt collecting in hydrophilic ether system oligomer which makes it dissolve in hydrophilic ether system oligomer using an organic solvent if needed beforehand, and mixes and dissolves the solution into a polysiloxane solution.

[0013] although the amount of the hydrophilic ether system oligomer used may be suitably determined according to the purpose of use etc. -- general -- per [10] polysiloxane 100 weight section - the 200 weight sections -- it considers as the 20 - 100 weight section above all Moreover, the amount of the alkali-metal salt used can also be suitably determined according to the ionic conductivity made into the purpose, and, generally per hydrophilic ether system oligomer 100 weight section and 1 - 50 weight section are used. The thickness to form is arbitrary and is 10-500 micrometers usually. The obtained film can be used for formation of various products, such as a cell, as a solid electrolyte.

[0014] Set to the general formula (I) described above example 1. For R1, in a phenyl group, R2 is [the polymerization degree (m) of a polyethylene-oxide portion] the end methylation polyethylene-oxide machine of 2, 4, 6, or 8. Weight-average-molecular-weight about 2 million polysiloxane whose number of polymerizations of the portion which has R2 (y) the number of polymerizations of the portion which has R1 (x) is 3, and is 1 is dissolved in a dimethylacetamide. Carry out churning mixture of the viscous solution of the ethylene oxide oligomer of LiClO4 content, and a uniform solution is prepared so that it may become this per polysiloxane 100 weight section with the blending

ratio of coal of the ethylene oxide oligomer (weight average molecular weight 400 [about]) of 30 weight sections, 60 weight sections, or the 100 weight sections. The film with a thickness of 50 micrometers was formed by the KYASUTENGU method, and the solid electrolyte was obtained. In addition, the amount from which the atomic ratio of O/Li in ethylene oxide oligomer is set to 10 was used for LiClO₄.

[0015] Set to the general formula (I) which carried out the example above of comparison. The number of polymerizations of the portion which has R1 (x) is 0, therefore consists only of a portion which has R2. Weight-average-molecular-weight about 2 million polysiloxane whose polymerization degree (m) of the polyethylene-oxide portion is the end methylation polyethylene-oxide machine of 2, 4, 6, or 8 is dissolved in a dimethylacetamide. Churning mixture of LiClO₄ was carried out, the uniform solution was prepared so that the atomic ratio of O/Li in the polyethylene oxide of R2 introduced into the polysiloxane at it might be set to 10, and according to the example 1, the solid electrolyte was obtained using it. Therefore, this thing does not contain ethylene oxide oligomer.

[0016] Ionic conductivity was measured with the alternating current impedance analyzer about the solid electrolyte obtained in the evaluation examination example 1 and the example of comparison. The result was shown in Table 1. In addition, A/B of front Naka means the rate of a polysiloxane / ethylene oxide oligomer. Moreover, the polymerization degree of an introductory polyethylene oxide means the polymerization degree of the polyethylene-oxide portion in the end methylation polyethylene-oxide machine introduced into the polysiloxane.

[0017]

[Table 1]

イオン伝導度 (S/cm; 25℃)					
	A/B	導入ポリエチレンオキシドの重合度			
		2	4	6	8
実施例1	10/3	1/10 ⁶	5/10 ⁶	1/10 ⁵	2/10 ⁴
	10/6	8/10 ⁶	1/10 ⁵	1/10 ⁴	1/10 ³
	10/10	1/10 ⁵	4/10 ⁵	6/10 ⁴	7/10 ³
比較例	10/0	2/10 ⁷	6/10 ⁷	3/10 ⁶	2/10 ⁵

[0018]

[Effect of the Invention] According to this invention, the polysiloxane film of micro phase separation structure can be formed, the hydrophilic phase can be made to be able to hold the ether system oligomer of alkali-metal salt content, and the solid electrolyte by which the quality which is excellent in ionic conductivity was stabilized can be obtained.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL FIELD

[Industrial Application] this invention is excellent in ionic conductivity, and relates to the suitable solid electrolyte for formation of a thin shape cell etc.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] Conventionally, the solid electrolyte which makes it come to contain an alkali-metal salt in the film which consists of a poly methyl siloxane to which the oligomer of ethylene oxide was introduced into the side chain was known. However, the trouble of being inferior to ionic conductivity is *****.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, the polysiloxane film of micro phase separation structure can be formed, the hydrophilic phase can be made to be able to hold the ether system oligomer of alkali-metal salt content, and the solid electrolyte by which the quality which is excellent in ionic conductivity was stabilized can be obtained.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] this invention makes a technical problem development of a solid electrolyte which consists of a film of the polysiloxane system by which was excellent in ionic conductivity and quality was stabilized.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] The solid electrolyte characterized by this invention containing the hydrophilic ether system oligomer of alkali-metal salt content in the film which consists of a polysiloxane which has a hydrophobic group and a hydrophilic group is offered.

[0005]

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

OPERATION

[Function] If the polysiloxane which has a hydrophobic group and a hydrophilic group is produced, the film which the hydrophobic group and hydrophilic group act and has micro phase separation structure can be formed, if this is made to contain the hydrophilic ether system oligomer of alkali-metal salt content, the film which holds the hydrophilic ether system oligomer of alkali-metal salt content in the hydrophilic phase in the micro phase separation structure in a film can be formed, and this film constitutes the solid electrolyte which is excellent in ionic conductivity. It is thought that the outstanding ionic conductivity is because the active segmental motion of the polysiloxane as matrix polymer, promotion of the ion transport by the hydrophilic group, and the ether system oligomer held by the micro domain exist continuously in sufficient space for an ion transport.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

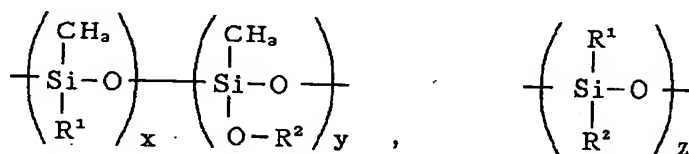
EXAMPLE

[Example] The solid electrolyte of this invention comes to have the hydrophilic ether system oligomer of alkali-metal salt content in the film of a polysiloxane system. As a polysiloxane which forms a film, what has a hydrophobic group and a hydrophilic group is used for a side chain.

[0007] What has the structural unit expressed with the following general formula (I) and (II) as an example of the aforementioned polysiloxane is raised. This polysiloxane can be formed by for example, the chemical polymerization method, the electrolytic polymerization method, etc., and although 20,000-8 million are common as for the average molecular weight, it is not limited to this.

(I)

(I I)



[0008] In the aforementioned general formula, R1 is a hydrophobic group which a carbon number becomes from three or more alkyl groups, phenyl groups, etc. R2 is a hydrophilic group which consists of an end methylation polyethylene-oxide machine, an end methylation polypropylene-oxide machine, an end methylation ethylene oxide propylene-oxide copolymer machine (a random copolymer, block copolymer), a hydroxyl group, a carboxyl group, an amino group, a sulfonic group, etc.

[0009] As the aforementioned hydrophilic group. The end methylation polyethylene-oxide machine expressed with -X-CH3 or -Y-CH3 (however, X is m (CH2CH2O) and Y is n (CH2CH(CH3)O).), an end methylation polypropylene-oxide machine or an end methylation ethylene oxide propylene-oxide copolymer machine, etc. is more desirable than points, such as improvement in the ionic conductivity by suppression of crystallization of ** and ether system polymer. In addition, although 2-20 are common as for the polymerization degree m and n of the polyethylene oxide in a formula, or a polypropylene oxide, it is not limited to this.

[0010] A thing proper as hydrophilic ether system oligomer of the alkali-metal salt content included in the film which consists of a polysiloxane can be used. As the example, ethylene oxide oligomer, propylene-oxide oligomer, ethylene oxide propylene-oxide copolymerization oligomer, etc. are raised. Although 100-2000 are common as for the average molecular weight of the hydrophilic ether system oligomer to be used, it is not limited to this.

[0011] As an example of an alkali-metal salt, what consists of combination with anions, such as cations, such as Li ion, Na ion, and K ion, I ion and CF3SO3 ion, BF4 ion, ClO4 ion, AlCl4 ion, PF6 ion, AsF6 ion, and SCN ion, is raised.

[0012] Formation of a solid electrolyte can dissolve the polysiloxane and the hydrophilic ether system oligomer which have a hydrophobic group and a hydrophilic group using the polar solvent like a dimethylacetamide, and an alkali-metal salt, and can be performed by producing a film by the method with a proper casting method etc. using the solution. In this case, an alkali-metal salt has the method

more desirable than the point of making an alkali-metal salt collecting in hydrophilic ether system oligomer which makes it dissolve in hydrophilic ether system oligomer using an organic solvent if needed beforehand, and mixes and dissolves the solution into a polysiloxane solution.

[0013] although the amount of the hydrophilic ether system oligomer used may be suitably determined according to the purpose of use etc. -- general -- per [10] polysiloxane 100 weight section - the 200 weight sections -- it considers as the 20 - 100 weight section above all Moreover, the amount of the alkali-metal salt used can also be suitably determined according to the ionic conductivity made into the purpose, and, generally per hydrophilic ether system oligomer 100 weight section and 1 - 50 weight section are used. The thickness to form is arbitrary and is 10-500 micrometers usually. The obtained film can be used for formation of various products, such as a cell, as a solid electrolyte.

[0014] Set to the general formula (I) described above example 1. For R1, in a phenyl group, R2 is [the polymerization degree (m) of a polyethylene-oxide portion] the end methylation polyethylene-oxide machine of 2, 4, 6, or 8. Weight-average-molecular-weight about 2 million polysiloxane whose number of polymerizations of the portion which has R2 (y) the number of polymerizations of the portion which has R1 (x) is 3, and is 1 is dissolved in a dimethylacetamide. Carry out churning mixture of the viscous solution of the ethylene oxide oligomer of LiClO₄ content, and a uniform solution is prepared so that it may become this per polysiloxane 100 weight section with the blending ratio of coal of the ethylene oxide oligomer (weight average molecular weight 400 [about]) of 30 weight sections, 60 weight sections, or the 100 weight sections. The film with a thickness of 50 micrometers was formed by the KYASUTENGU method, and the solid electrolyte was obtained. In addition, the amount from which the atomic ratio of O/Li in ethylene oxide oligomer is set to 10 was used for LiClO₄.

[0015] Set to the general formula (I) which carried out the example above of comparison. The number of polymerizations of the portion which has R1 (x) is 0, therefore consists only of a portion which has R2. Weight-average-molecular-weight about 2 million polysiloxane whose polymerization degree (m) of the polyethylene-oxide portion is the end methylation polyethylene-oxide machine of 2, 4, 6, or 8 is dissolved in a dimethylacetamide. Churning mixture of LiClO₄ was carried out, the uniform solution was prepared so that the atomic ratio of O/Li in the polyethylene oxide of R2 introduced into the polysiloxane at it might be set to 10, and according to the example 1, the solid electrolyte was obtained using it. Therefore, this thing does not contain ethylene oxide oligomer.

[0016] Ionic conductivity was measured with the alternating current impedance analyzer about the solid electrolyte obtained in the evaluation examination example 1 and the example of comparison. The result was shown in Table 1. In addition, A/B of front Naka means the rate of a polysiloxane / ethylene oxide oligomer. Moreover, the polymerization degree of an introductory polyethylene oxide means the polymerization degree of the polyethylene-oxide portion in the end methylation polyethylene-oxide machine introduced into the polysiloxane.

[0017]

[Table 1]

イオン伝導度 (S/cm; 25℃)					
	A/B	導入ポリエチレンオキシドの重合度			
		2	4	6	8
実施	10/3	1/10 ⁶	5/10 ⁶	1/10 ⁵	2/10 ⁴
	10/6	8/10 ⁶	1/10 ⁵	1/10 ⁴	1/10 ³

例 1	10/10	1/10 ⁵	4/10 ⁵	6/10 ⁴	7/10 ³
比較例	10/0	2/10 ⁷	6/10 ⁷	3/10 ⁶	2/10 ⁵

[Translation done.]